

Recent developments in the use of voltammetric solid state microelectrodes to understand diagenetic processes

G. W. Luther, III
M. Taillefert
A. Bono
P. J. Brendel

College of Marine Studies, University of Delaware, Lewes, DE
19958, USA

B. Sundby

INRS-Océanologie, Université du Québec, Rimouski, Québec
G5L 3A1, Canada

C. E. Reimers

Institute of Marine and Coastal Sciences, Rutgers University, New
Brunswick, NJ 08903, USA

D. B. Nuzzio

Analytical Instrument Systems, Inc., Flemington, NJ 08822, USA

D. Lovalvo

Eastern Oceanics, Inc., West Redding, CT 06896, USA

Microelectrodes were first applied to the study of sediment properties by Revsbech *et al.* (1980) who used a membrane type polarographic microelectrode to describe the distribution of dissolved O₂ in sediment pore water with sub-millimeter resolution. Because of their small size, microelectrodes can be used without destroying the sediment sample. In addition, they can be used to observe how the concentration of a species in the pore water varies in response to changes occurring at the sediment water interface as well as to examine solute transport in pore waters. A number of other analyte-specific membrane-type microelectrodes have been introduced, including electrodes for H₂S, N₂O (Revsbech *et al.*, 1988), and pH and pCO₂ (Cai and Reimers, 1993). Combination electrodes have been developed for O₂/N₂O (Revsbech *et al.*, 1988) and O₂/H₂S (Visscher *et al.*, 1991) but for the most part each electrode can only measure one species. The use of microelectrodes has had a profound impact on our understanding of dynamic processes within the uppermost few mm of the sediment, where many of the reactions that involve organic carbon mineralization take place.

There is strong interest in anaerobic sulphide oxidation by Fe and Mn oxide minerals and bacterial reduction of Fe and Mn (e.g. Aller, 1988). The first tool to determine dissolved Fe and Mn on (sub)millimeter scales was a gel diffusion technique (e.g. Davison *et al.*, 1994). In this method, the gel sampler is placed in the sediment and porewater constituents diffuse into the gel. After allowing sufficient time for equilibrium to be established between the gel and the pore water, the sampler is

carefully removed and subsampled by cutting the gel into thin sections. The analyte of interest is then leached from the gel sections and analysed. The gel technique has so far not provided measurements of O₂ and H₂S.

A solid state Au/Hg voltammetric microelectrode that can measure rapidly, at the same time, and with (sub)millimeter spatial resolution, five of the principal redox species involved in early diagenesis (O₂, Mn²⁺, Fe²⁺, HS⁻, and I⁻) as well as FeS and Fe(III) species was developed by Brendel and Luther (1995). This tool can be used to measure the distribution of these redox components in the porewaters of marine and freshwater sediments as well as temporal changes at any given depth.

Results and discussion

The solid-state microelectrode has now been used *in situ* to measure pore water profiles of dissolved O₂, Mn, Fe, and sulphide at a 10 m deep site in Raritan Bay, N.J. The voltammetric sensor was positioned and manipulated with microprofiling instrumentation mounted on a small Remote Operated Vehicle (ROV). The electrode was connected to the shipboard voltammetric analyser with a 30 m cable which had receiver-transmitter transducers on each end to preserve the signal quality along the cable. The sensor was thus controlled and monitored in real-time from the research vessel anchored at the study site. Single analyte O₂, pH and resistivity microsensors were inserted into the sediment next to the voltammetric sensor. We report the concentration changes of redox species observed from 2–3 cm

above the sediment-water interface to approximately 4 cm below. The profiles (e.g. Fig. 1) show no detectable overlap of O_2 and Mn^{2+} in the sediments similar to observations on cores from other continental margin sites. In one dive a subsurface Mn^{2+} peak was observed at about 2 cm and coincided with a subsurface pH maximum. The data can be explained by organic matter decomposition with alternative electron acceptors and by secondary reactions involving the products from organic matter decomposition.

In many of the porewater studies to date, we have observed a broad signal for Fe(III) species. Comparison of this signal with several laboratory prepared Fe(III) organic complexes indicates that the porewater signal represents Fe(III) organic complexes. On ageing, the Fe(III) signal shifts from about -0.4 V to more negative potentials. The Fe(III) signal is not observed when sulphide is present in porewaters and known Fe(III) complexes are shown to react with sulphide in a matter of minutes.

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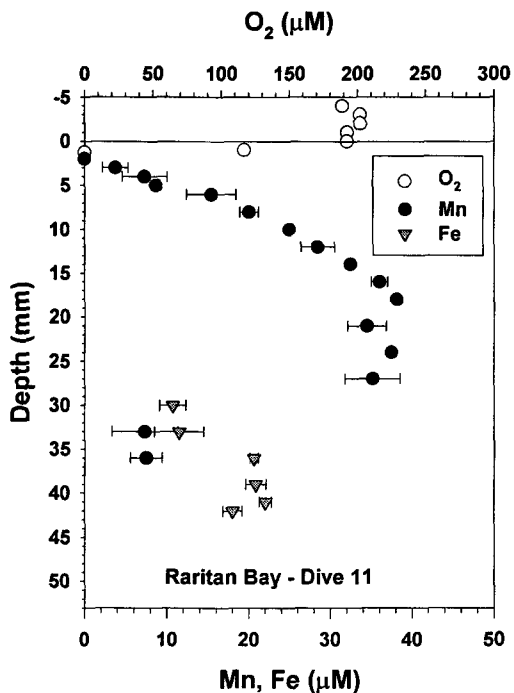


FIG. 1. Distribution of dissolved O_2 , Mn and Fe in porewaters from Raritan Bay New Jersey. O_2 and Mn do not overlap. O_2 is not detected at 2 mm depth and Mn is first detected at 3 mm.

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